
**STUDIES OF CONDUCTION MECHANISMS IN A HEAVILY
Co-DOPED n -TiNiSn INTERMETALLIC SEMICONDUCTOR****V.A. ROMAKA^{1,2}, YU.V. STADNYK³, K.A. REVENKO², D. FRUCHART⁴,
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Temperature dependences of the specific electroresistance, Seebeck coefficient, and structural characteristics of a heavily Co-doped ($N^{\text{Co}} = 9.5 \times 10^{19} \div 1.9 \times 10^{21} \text{ cm}^{-3}$) n -TiNiSn intermetallic semiconductor, $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$, have been studied in the temperature range $T = 80 \div 380 \text{ K}$. The corresponding electron density of states (DOS) has been calculated. Co atoms, at concentrations $x < 0.03$, were found to occupy the crystallographic positions of Ti and Ni ones with different occupation numbers and act as defects of the donor or acceptor nature, respectively.

1. Introduction

This work continues our previous studies [1–4] of the conditions, under which the generation of donor or acceptor defects occurs in doped intermetallic semiconductors. Our researches of the influence of doping impurities on electrokinetic, magnetic, structural, and energy characteristics of p -TiCoSb, n -ZrNiSn, and n -TiNiSn revealed different behavior of impurities inserted into the crystalline structure of those semiconductors. Our experimental studies [1] showed that impurity atoms can occupy different crystallographic positions, because there are vacancies in the p -TiCoSb, n -ZrNiSn, and n -TiNiSn structures. Namely, in p -TiCoSb, the crystallographic positions of Ti and Co atoms are filled to 93.3 and 95.8%, respectively; in n -ZrNiSn, the positions of Zr and Ni

atoms are filled to 90.0 and 91.6%, respectively; and in n -TiNiSn, the positions of Ti and Ni atoms are filled to 94.0 and 95.6%, respectively. Hence, there appears an opportunity for impurity atoms – being under favorable conditions – to simultaneously occupy different vacant crystallographic positions.

For instance, if p -TiCoSb is doped with V impurity atoms, the latter simultaneously occupy the positions of Ti and Co atoms with different occupation degrees. Since V is an acceptor with respect to Co and a donor with respect to Ti, the insertion of V into the p -TiCoSb structure is accompanied by the simultaneous generation of nonequivalent numbers of donor and acceptor defects. At the same time, during the doping of p -TiCoSb with Ni and Cu donor impurities, the impurity atoms occupy only crystallographic Co positions and generate donor defects [3, 4]. In a similar manner, Sc atoms enter into the n -TiNiSn structure, occupy the positions of Ti atoms, and generate acceptor defects [2]. The described insertion of impurity atoms into the crystalline structure of a semiconductor is accompanied by the variations of its compensation degree and changes the behavior of its electrokinetic characteristics.

In work [1], the assumption was made that “the dimensional factor”, i.e. the ratio between the radii of the semiconductor basic matrix atoms and the impurity ones, is crucial for determining which crystallographic

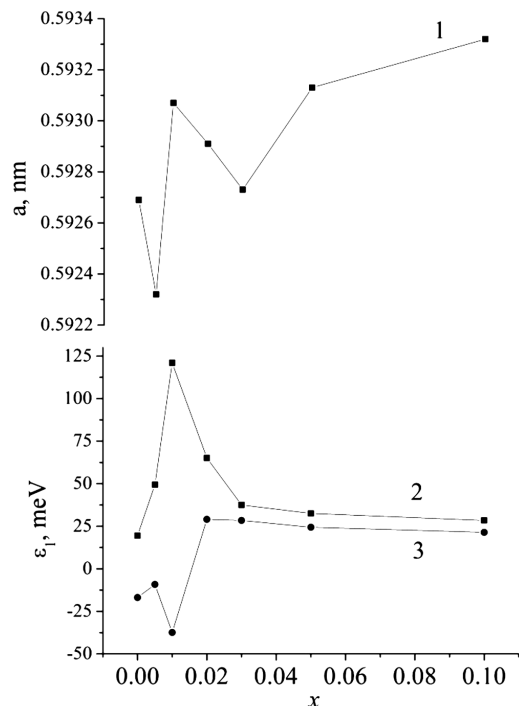


Fig. 1. Impurity-concentration dependences of the elementary cell period (1), and the activation energies ε_1^α (2) and ε_1^β (3) in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$

positions will be occupied by the latter. For instance, when p -TiCoSb is doped with V atoms, the ratios between the atomic radii are $r_{\text{Ti}}/r_{\text{V}} = 1.09$ and $r_{\text{Co}}/r_{\text{V}} = 0.93$, so that V atoms simultaneously and equivalently occupy the positions of Ti and Co atoms. In the case of p -TiCoSb doping with Ni and Cu atoms, the ratios between the atomic radii are $r_{\text{Ti}}/r_{\text{Ni}} = 1.17$, $r_{\text{Ti}}/r_{\text{Cu}} = 1.14$, $r_{\text{Co}}/r_{\text{Ni}} = 1.00$, and $r_{\text{Co}}/r_{\text{Cu}} = 1.17$; and Ni and Cu atoms occupy only the crystallographic positions of Co atoms, which are close to them by the atomic radius. At the same time, in the case where n -TiNiSn is doped with Sc, impurity atoms occupy only the positions of Ti atoms, close to Sc ones by the atomic radius: $r_{\text{Ti}}/r_{\text{Sc}} = 0.90$ and $r_{\text{Ni}}/r_{\text{Sc}} = 0.76$.

The search for the reasons of why the defects of donor and/or acceptor nature are generated simultaneously, when intermetallic semiconductors are doped, will allow us to understand more comprehensively the conditions that are required for the fabrication of thermoelectric materials with improved metrologic characteristics [5]. In this context, interesting are the results of the doping of n -TiNiSn with atoms, the radii of which are considerably smaller than the radius of Sc impurity atoms studied before.

In this work, we report the results of our researches concerning the influence of a Co impurity on the structural, electrokinetic, and energy characteristics of n -TiNiSn. We measured the temperature dependences of the specific electroresistance ρ , the thermal emf coefficient α , and some structural characteristics. We also calculated the DOS distribution in n -TiNiSn heavily doped with a Co ($3d^74s^2$) impurity, which substitutes Ni ($3d^84s^2$) atoms; the radius ratios are $r_{\text{Ti}}/r_{\text{Co}} = 1.17$ and $r_{\text{Ni}}/r_{\text{Co}} = 0.99$. The impurity concentration N^{Co} was varied from $9.5 \times 10^{19} \text{ cm}^{-3}$ (at $x = 0.005$) to $1.9 \times 10^{12} \text{ cm}^{-3}$ (at $x = 0.10$). The technique of specimen fabrication, the regimes of homogenizing annealing and X-ray diffraction researches, the procedure of DOS calculations in the framework of the self-consistent Korringa–Kohn–Rostoker method, using the coherent potential approximation (KKR–CPA–LDA), and the techniques applied for measuring the specific electroresistance and the thermal emf coefficient with respect to copper in the temperature interval 80–380 K were described in work [1].

2. Studies of the Crystalline Structure of and the Electron DOS in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$

The structural researches aimed at finding the variant of atomic arrangement (or atomic absence) over the sites of an elementary cell in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$, at which the Bragg factor of correspondence between the model representation of the crystalline structure and the X-ray diffraction experimental results was minimal [6]. Taking into account that the atomic radius of Co ($r_{\text{Co}} = 0.1252 \text{ nm}$) is insignificantly larger than that of Ni ($r_{\text{Ni}} = 0.1246 \text{ nm}$), a slight increase of the $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ elementary cell period was expected. However, the introduction of even the lowest concentration of a Co impurity gave rise to a drastic reduction of the period value (see Fig. 1, curve 1). Then, this quantity drastically increased in the impurity concentration interval $x = 0.005 \div 0.01$, decreased in the interval $x = 0.01 \div 0.03$, and increased again at $x > 0.03$.

To elucidate the origins of such a behavior of $\alpha(x)$ in more details, we studied interatomic distances in the crystalline structure of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ and the occupation numbers of crystallographic atomic positions. Within four conditional impurity concentration intervals ($x = 0 - 0.005$, $x = 0.005 - 0.01$, $x = 0.01 - 0.03$, and $x > 0.03$), Co impurity atoms occupied—simultaneously and with different occupation numbers—the crystallographic positions of both Ti and Ni atoms. The lattice period either diminished or became

larger, depending on whether Co atoms mostly occupied the crystallographic positions of Ti or Ni ones.

Co atoms are donors with respect to Ti ones and acceptors with respect to Ni ones. Therefore, the doping of n -TiNiSn with a Co impurity is accompanied by the simultaneous introduction of both donor and acceptor defects, and the relationship between those defects depends on to what extent the vacant Ti and Ni positions are occupied. Such a character of the simultaneous generation of donor and acceptor defects in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ has to reveal itself in the electrokinetic characteristics of the semiconductor.

The DOS calculations were carried out supposing that Co impurity atoms occupy both the Ni and Ti crystallographic positions. From the results of calculations exhibited in Fig. 2, it follows that n -TiNiSn is a semiconductor, in which the energy gap ε_g between the conduction and valence bands is formed as a result of the strong hybridization between the d -states of transition elements Ti and Ni: the DOS in the conduction band is mainly governed by Ti's d -states, while the DOS in the valence band by Ni's d -states, which overlap with Ti's d -states and Sn's p -states. The Fermi level in n -TiNiSn, like in the n -ZrNiSn case, is located in the energy gap, near the bottom of the conduction band, which should give rise to the negative sign of the thermal emf coefficient in experiment.

The results of calculations concerning the contribution to DOS given by each component of the solid $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ solution and the total DOS at various x -values testify that the substitution of Ti or Ni atoms by Co ones does not change the observed DOS profile, and that $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ remains a semiconductor solid solution.

The doping of n -TiNiSn with an acceptor Co impurity (Co atoms preferably occupy Ni crystallographic positions) was accompanied by the intensity variation of the valence- and conduction-band peaks and by the drift of the Fermi level toward the valence band (Fig. 2), which should stimulate a change of the majority carrier type (the change of the sign of the thermal emf coefficient). In experiment, a reduction of the energy of activation from the Fermi level onto the percolation level in the valence band of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ should take place. As early as at $x = 0.1$, the Fermi level crosses the percolation level in the valence band, and the electroconductivity of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ acquires the metallic character.

Thus, the doping of the intermetallic semiconductor n -TiNiSn with a Co impurity is accompanied by the variation of the compensation degree which is

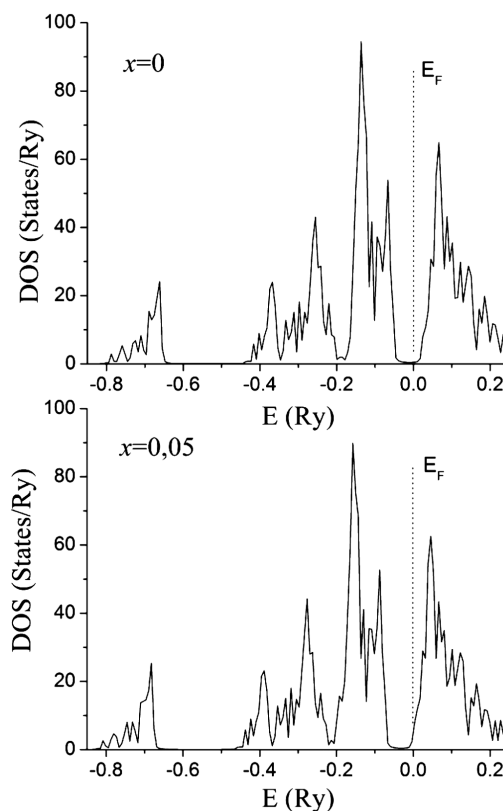


Fig. 2. Calculated DOS in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$

characterized by rather a complicated behavior, by the change of the majority carrier type at $x \approx 0.01$, and by a monotonous drift of the Fermi level toward the valence band, followed by the intersection of the percolation level in the valence band and the implementation of the insulator-metal transition (the Anderson transition [7]).

3. Electrokinetic Studies of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$

The temperature dependences of the specific electroresistance in $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ are typical of semiconductors: the corresponding values diminish with the temperature growth, and the dependences $\ln \rho(1/T)$ contain high-temperature activation sections (Fig. 3) associated with the activation of charge carriers into continuous energy bands. At the same time, only two $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ specimens (with $x = 0$ and 0.05) demonstrated the $\ln \rho(1/T)$ -dependences that contained a high-temperature activation section associated with the hopping conductivity through localized states. The absence of low-temperature activation sections and the presence of extrema in the dependences $\ln \rho(1/T)$

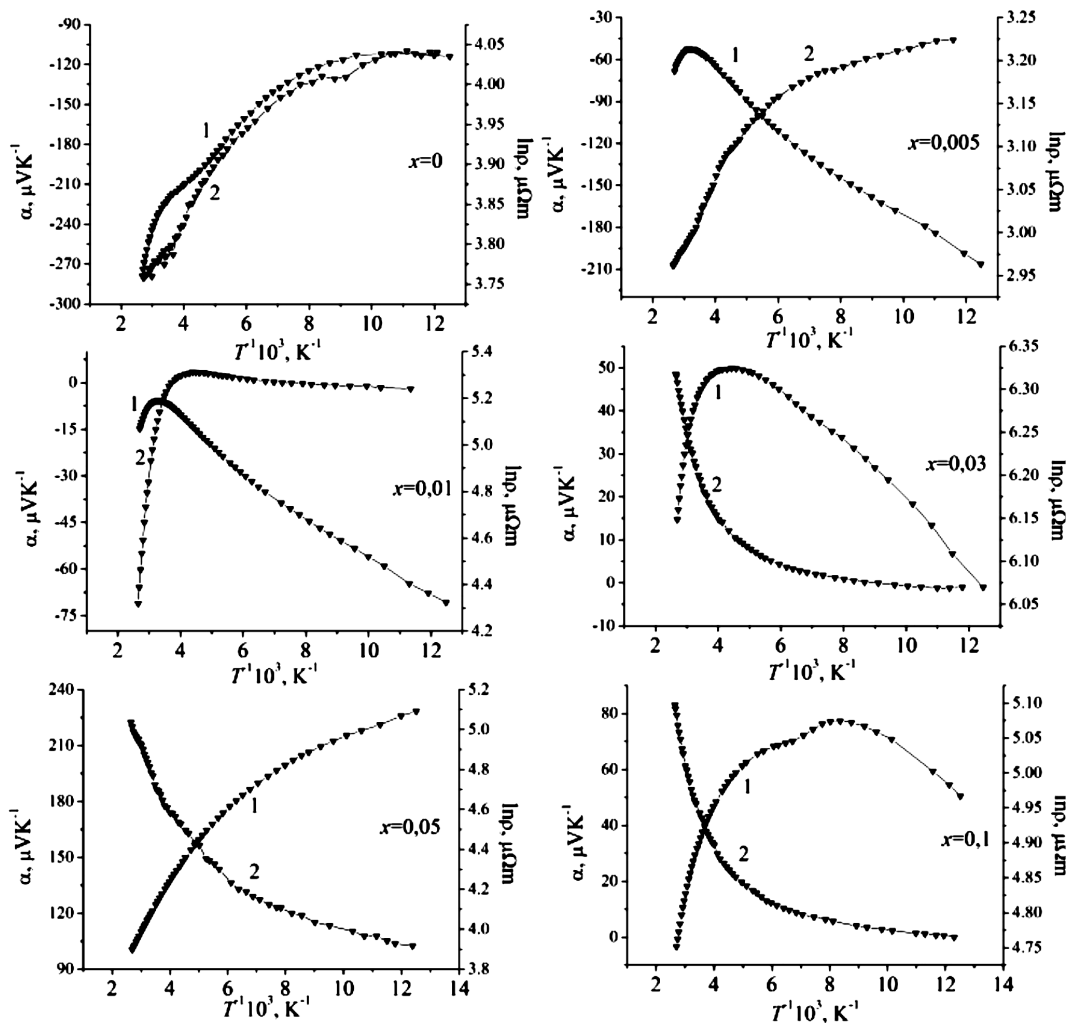


Fig. 3. Temperature dependences of the specific electroresistance (1) and the thermal emf coefficient (2) of TiNi_{1-x}Co_xSn

evidence for the metallization of the conductivity through localized states due to considerable impurity concentrations and a small depth of the potential well of small-scale fluctuations (a fine structure of large-scale fluctuations).

The temperature dependence $\alpha(1/T)$ of the thermal emf coefficient of TiNi_{1-x}Co_xSn (see Fig. 3) also reveals features inherent to semiconductors – high- and low-temperature activation sections which can be approximated by the dependence

$$\alpha = \frac{k}{e} \left(\frac{\varepsilon_1^\alpha}{kT} - \gamma + 1 \right),$$

where γ is a parameter that depends on the scattering nature and, in the *n*-TiNiSn case, amounts to 1.03. For all specimens under investigation, by analyzing the

high-temperature sections in the dependences $\ln \rho(1/T)$ and $\alpha(1/T)$, and using the formula for the thermal emf coefficient given above, we calculated the values of the activation energies ε_1^ρ and ε_1^α , respectively (Fig. 1). In the case of conventional semiconductors, those energies give the energy barrier between the Fermi level and the percolation level in the corresponding continuous energy band. Note that the amplitude of this barrier does not depend on how it is measured. As follows from Fig. 1, the activation energies ε_1^ρ and ε_1^α are quite different, which – in view of the results of structural researches of TiNi_{1-x}Co_xSn – testifies to the presence of local amorphization (fluctuations of the content) [7] and fluctuations of charged impurities [8] in the specimens, and – as a consequence – the fluctuations of continuous energy bands [9]. That is why the traditional approaches,

which are used to analyze weakly doped semiconductors, are unacceptable in this case.

Insertion of a Co impurity with the lowest concentration that was accessible in experiments was accompanied by a reduction of the specific electroresistance (Fig. 4), in particular, from $\rho_{x=0} = 43.3 \mu\Omega \times \text{m}$ to $\rho_{x=0.005} = 24.2 \mu\Omega \times \text{m}$ at $T = 80 \text{ K}$. Such a behavior of the dependence $\rho(x)$ in the interval $x = 0 - 0.005$ evidences for an increase of the DOS at the Fermi level; it can be implemented only if a donor impurity was introduced into n -TiNiSn. The growth of electroconductivity in the interval $x = 0 - 0.005$ can be associated with an increase of the free electron concentration by means of their thermally induced throwing from the Fermi level into the conduction band ($\sigma(\varepsilon) \sim n(\varepsilon)$). If it is so, the Fermi level has to drift toward the conduction band. The behavior of the dependence $\rho(x)$ in the interval $x = 0 - 0.005$ confirms the conclusions drawn on the basis of X-ray diffraction researches that, in this concentration range, Co atoms preferably occupy the positions of Ti atoms and act as a donor impurity. The change of the thermal emf coefficient of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ confirms our assumption about different characters of Co impurities inserted into the crystalline structure of the intermetallic semiconductor. The fact that Co atoms act as donor defects in the interval $x = 0 - 0.005$ is justified by the negative values of the thermal emf coefficient.

This conclusion is also confirmed by Fig. 1 which illustrates how the energy ε_1^ρ of activation from the Fermi level onto the percolation levels in the continuous energy bands changes, when the Co impurity concentration in n -TiNiSn varies. Insertion of a Co impurity with the lowest concentration is accompanied by a drift of the Fermi level toward the conduction band from the values $\varepsilon_1^\rho(x=0) = 16.9 \text{ meV}$ to $\varepsilon_1^\rho(x=0.005) = 9.2 \text{ meV}$. Different ε_1^ρ -signs in Fig. 1 correspond to different activation mechanisms of charge carriers: sign “minus” corresponds to the activation of electrons from the donor level into the conduction band, while sign “plus” does to the activation of holes into the valence band.

The increase of the specific electroresistance of $\text{TiNi}_{1-x}\text{Co}_x\text{Sn}$ in the concentration interval $x = 0.005 - 0.02$ can be related to a reduction of the free electron concentration; in so doing, the Fermi level moves away from the percolation level in the conduction band (from $\varepsilon_1^\rho(x=0.005) = 9.2 \text{ meV}$ to $\varepsilon_1^\rho(x=0.01) = 37.4 \text{ meV}$). A reduction of the electron concentration and a simultaneous increase of the hole concentration in the interval $x = 0.005 - 0.01$ are accompanied by an

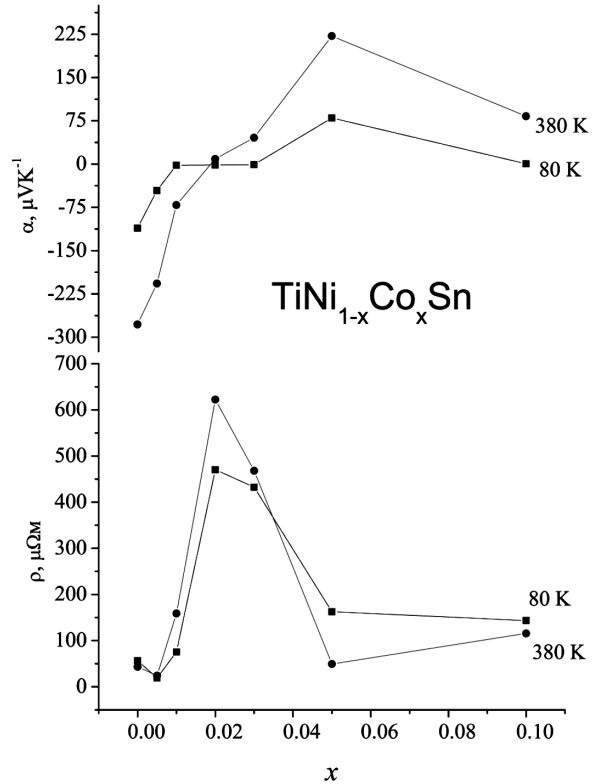


Fig. 4. Impurity-concentration dependences of the thermal emf coefficient and the specific electroresistance in $\text{ZrNi}_{1-x}\text{Fe}_x\text{Sn}$

increase of the compensation degree in the semiconductor, which – in accordance with the Shklovskii–Efros model for a heavily doped compensated semiconductor – gives rise to a substantial growth of the large-scale fluctuation amplitude [8, 9]. As follows from Fig. 1, the quantity ε_1^α has its maximal values just in this concentration interval. In the impurity concentration range $x = 0.01 - 0.02$, the Fermi level intersects the middle of the energy gap and approaches the percolation level in the valence band to the distance $\varepsilon_1^\rho(x=0.02) = 29.1 \text{ meV}$. In particular, it is evidenced for by the change of the sign of the thermal emf coefficient (Figs. 3 and 4).

Since the specimens under investigation are heavily doped and strongly compensated, the increase of both the acceptor defect concentration and the contribution of free holes to the conductivity should manifest itself as the inversion of the sign of the thermal emf coefficient at lower temperatures T_{inv} , which is an extra confirmation of the Fermi level drift toward the valence band (Fig. 5). An almost linear character of the dependence $T_{\text{inv}}(x)$

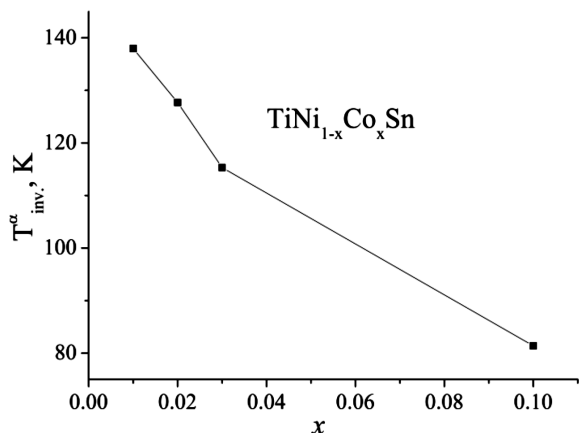


Fig. 5. Impurity-concentration dependence of the temperature T_{inv}^α , at which the thermal emf coefficient of $TiNi_{1-x}Co_xSn$ changes its sign

testifies to the same character of the Fermi level shift toward of the valence band in $TiNi_{1-x}Co_xSn$.

The decline of the dependence $\rho(x)$ for $TiNi_{1-x}Co_xSn$ at $x > 0.02$ can be explained by an increase of both the free hole concentration and the DOS at the Fermi level, when the latter approaches the percolation level in the valence band. Analyzing the dependences $\rho(x)$ and $\alpha(x)$, we may suppose that Co atoms behave as an acceptor impurity in this impurity concentration range, which is confirmed by structural researches. The overcompensation and the increase of the acceptor impurity concentration in the semiconductor – now, with the hole type of conductivity – give rise to a reduction of the compensation degree and a decline of the dependence $\varepsilon_1^\alpha(x)$ (Fig. 1).

4. Conclusions

So, the insertion of Co atoms into the crystalline structure of $n-TiNiSn$ is accompanied by the simultaneous substitution of Ni and Ti atoms; however, the effectiveness of such a procedure depends on the concentration of Co atoms. We suppose that the mechanism of simultaneous substitution of several different atomic positions in the crystalline structure of the intermetallic semiconductor by atoms of the same kind is responsible for the simultaneous generation of defects belonging to different types. The concentrations of those defects and the corresponding concentration ratios change as well, which manifests itself in the electrokinetic characteristics of the semiconductor.

The position of the Fermi level in $TiNi_{1-x}Co_xSn$ is governed by an extent, to which Co atoms substitute Ni and Ti ones; at the same time, Co atoms are chaotically distributed in the crystalline structure of the intermetallic semiconductor $TiNi_{1-x}Co_xSn$.

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ДОСЛІДЖЕННЯ ПРОВІДНОСТІ ІНТЕРМЕТАЛІЧНОГО НАПІВПРОВІДНИКА $n-TiNiSn$, СИЛЬНОЛЕГОВАНОГО ДОМІШКОЮ Co

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Резюме

Досліджено температурні залежності питомого електроопору, коефіцієнта термо-ерс, структурні характеристики, а також здійснено розрахунок розподілу щільності електронних станів (DOS) інтерметалічного напівпровідника $n-TiNiSn$, сильнолегованого домішкою Co ($N^{Co} = 9,5 \cdot 10^{19} \div 1,9 \cdot 10^{21} \text{ см}^{-3}$), у температурному діапазоні $T = 80 \div 380 \text{ К}$. Показано, що при концентраціях $x < 0,03$ атоми Co одночасно у різних співвідношеннях займають кристалографічні позиції атомів Ti та Ni, виступаючи дефектами донорної та акцепторної природи відповідно.